

Synthetic Lubricants

Edited by

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CHAPTER I

Introduction

REIGH C. GUNDERSON*

The twentieth century has brought into being many major advances in the fields of industry, science and transportation. With each step forward, numerous materials problems arose. Among these, the problems of providing adequate lubrication under new and extreme conditions assumed great importance, leading to the development of synthetic lubricants.

The field of synthetic lubricants has expanded greatly in recent years. Many types have been developed to meet today's needs, and research on new materials for tomorrow is extensive and continuing at an ever-accelerating pace.

One natural result of such extensive research has been a proliferation of publications on synthetic lubricants, particularly—in view of their many military uses—of government research reports. At the same time, the rapidly developing and changing technology has until now discouraged efforts to report over-all developments in any detailed fashion. At present, therefore, persons wishing to gain a general understanding of one or more groups of synthetic lubricants can do so only by consulting a wide array of articles, bulletins and reports, many of which are not readily accessible.

Undesirable practical consequences can follow. For example, it is frequently true that several groups of synthetic lubricants can perform adequately in a particular piece of equipment or application. Too often, however, the lubricant utilized is selected merely because of the aggressive sales efforts of the producers, rather than because it is the best of several possible choices. In some installations, mineral-oil lubricants may be used where a synthetic would be preferable.

This volume seeks to correct the present situation. It provides comprehensive discussions of the synthetic lubricant types that are currently produced on a commercial scale, or are in a developmental stage sufficiently

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CHAPTER 4

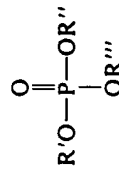
Phosphate Esters

ROGER E. HATTON*

INTRODUCTION

The incorporation of phosphorus into organic molecules results in materials of unusual and interesting properties. Many classes of organophosphorus compounds exist and each has its own characteristics. Of these classes, the phosphate esters have properties making them especially useful as lubricants. The chemistry, the properties, and the lubricant uses of the orthophosphate esters are discussed in this chapter.

The structure of the orthophosphate esters may be represented as:



where at least one R represents an organic group while the remaining represent organic groups or hydrogen atoms. The R groups may be the same or may be different. For example, a triaryl phosphate may contain three identical aryl groups as in triphenyl phosphate or the aryl groups may be different as in phenyl-*m*-tolyl-*p*-chlorophenyl phosphate.

The tertiary phosphate esters are often classified as triaryl phosphates, trialkyl phosphates, and alkyl aryl phosphates. These groupings will be used in this chapter since the properties of the esters are determined primarily by the organic portion of the molecule.

In addition to the neutral or tertiary phosphate esters in which all three R's are organic radicals, compounds in which one or two of the R's are hydrogen are known. Thus, (R'O)P(O)(OH)₂ is a primary phosphate ester and (R'O)(R''O)P(O)OH is a secondary phosphate ester. Again, R' and R'' in the preceding formulas can be any organic group. These compounds

*Monsanto Chemical Company

are also commonly called organic substituted phosphoric acids or partial esters of phosphoric acid.

The primary and secondary phosphates have found little use as the major constituent of synthetic lubricants. Their major utility in lubricants is as additives in the form of the acids, the salts or the amides. These additives are claimed to function as rust inhibitors, lubrication improvers, stabilizers, antioxidants and corrosion inhibitors.

Sulfur analogs of the compounds discussed above are also well known. The affix "thio" is used for those compounds in which sulfur has replaced oxygen in the ROP or HOP linkage and "thiono" is used if sulfur has replaced oxygen in the P(O) linkage. The affix "thio" can be used for either replacement and is used unless there is definite proof of structure.

The thiophosphates, like the primary and secondary phosphates, are used as additives rather than as the major constituent of synthetic lubricants. Many thiophosphates and thiophosphate derivatives are well known and have achieved considerable commercial importance. They serve as lubrication additives performing film-strengthening, anti-wear, and extreme pressure functions and as antioxidants, corrosion inhibitors and stabilizers.

The tertiary phosphate esters have also found use as lubrication additives, principally as anti-wear agents. However, these esters have demonstrated utility as synthetic lubricants, *per se*, and further discussion will be limited to the tertiary orthophosphate esters.

HISTORY

The chemical history of the orthophosphate esters is old and well established. Trialkyl phosphates were prepared at least one hundred years ago⁸⁸ and triphenyl phosphate was synthesized as early as 1854.⁸⁹ However, phosphate esters did not begin to attract industrial interest until some time in the early 1920's when an attempt was made to find substitute plasticizers for cellulose nitrate in order to break the camphor monopoly held by the Japanese.

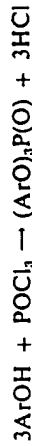
In the past several years, the tertiary phosphate esters have become important commercial chemicals. They have found uses as plasticizers, anti-foam agents, oil additives, combustion engine fuel additives, fire-resistant hydraulic fluids, and synthetic lubricants.

PREPARATION

Preparation of the tertiary phosphate esters can best be described by considering three separate types—the triaryl, the trialkyl, and the alkyl aryl phosphates.

TRIARYL PHOSPHATES

The simplest method of preparing triaryl phosphates involves the reaction of a phenolic compound with phosphorus oxychloride, as indicated below.

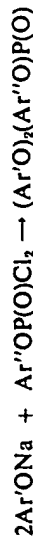


The hydrogen chloride may be removed by reaction with a tertiary organic base such as pyridine, by evacuation, by heating, or by passing an inert gas through the reaction mixture. The reaction is generally carried out at elevated temperatures (up to 400° F) and in the presence of catalysts such as aluminum chloride, magnesium chloride, etc. The patent literature describes many variations of this basic procedure. A slight excess of the phenolic compound is often employed in order to minimize formation of $(\text{ArO})_2\text{ClP(O)}$ and $(\text{ArO})\text{Cl}_2\text{P(O)}$. The reaction product may be washed with aqueous alkaline solutions to remove both the excess phenolic materials and the partial esters resulting from hydrolysis of the corresponding chloro derivatives.

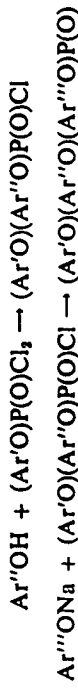
A commercial process for making tricresyl phosphate has recently been described.⁴⁷ The crude tricresyl phosphate is produced by the reaction of cresylic acid and phosphorus oxychloride at about 500° F. The resulting hydrogen chloride is removed by reduced pressure. The crude product is distilled to remove cresylic acid, washed with aqueous alkali and with water, and then dehydrated under vacuum. Filtration gives the finished product.

Tricresyl phosphate is the most widely used triaryl phosphate. However, the name "tricresyl phosphate" as normally used refers to a mixture of triaryl phosphates made from cresylic acid. The term "cresylic acid" identifies a wide variety of phenolic materials derived from both coal tar and petroleum. By selection of type and source of cresylic acid, so-called tricresyl phosphates possessing a wide range of physical and chemical properties may be prepared.

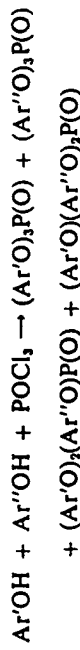
Triaryl phosphates containing two or three different substituents can be made stepwise by the reaction of a sodium phenoxide with an aryl phosphoryl chloride as shown in the following:



The phosphoryl chlorides can be synthesized by reaction of a phenolic compound and phosphorus oxychloride and isolated by distillation. This scheme can also be extended as shown below.



Mixtures of triaryl phosphates which result from using mixtures of phenolic materials in the reaction with phosphorus oxychloride are:



The properties of the mixture prepared as indicated above approximate those of a mixture of symmetrical triaryl phosphates in which the over-all ratio of aryl groups is the same.

TRIALKYL PHOSPHATES

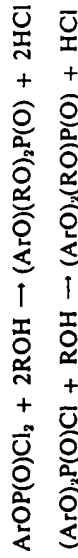
The formation of trialkyl phosphates from alcohols and phosphorus oxychloride requires a set of conditions quite different from those needed to prepare the aryl derivatives. Principal differences are as follows: The reaction temperature should be kept moderate, a substantial excess of alcohol should be used, and means should be provided for the rapid removal of hydrogen chloride. The latter may be accomplished by the addition of a tertiary organic base or dry ammonia, by prolonged evacuation with stirring or by blowing with an inert gas. Catalysts can be used to facilitate reaction. The higher molecular weight trialkyl phosphates may be purified by aqueous alkali and water washing, removal of the excess alcohol and distillation of the trialkyl ester. Dry refining techniques are required for the lower molecular weight trialkyl phosphates because of their solubility in water.

Many other ways of making the trialkyl phosphates have been proposed. These include the reaction of sodium alkoxides with phosphorus oxychloride and the reaction of silver phosphate with an alkyl halide. The literature contains numerous examples of other procedures which are beyond the scope of this chapter.

The preparation of trialkyl phosphates containing two or three different alkyl groups can be accomplished by the use of mixed alcohols with phosphorus oxychloride or by the sodium alkoxide route. Considerations similar to those discussed for the triaryl phosphates hold for these trialkyl phosphates.

ALKYL ARYL PHOSPHATES

This class of phosphate esters includes two groups, the alkyl diaryl phosphates and the dialkyl aryl phosphates. Both may be made by the general procedure given below.



The aryl phosphoryl dichloride or diaryl phosphoryl chloride can be prepared by the reaction of phosphorus oxychloride and a phenolic compound followed by separation of the desired material by distillation. The reaction with the alcohol is then carried out in a manner similar to that described for trialkyl phosphate preparation. Obviously, sodium alcoholates can be used in place of the alcohols.

A convenient method for the preparation of primary alkyl diaryl phosphates consists of the reaction of an alkyl phosphoryl chloride with sodium arylate as shown hereunder.³⁵



When primary alcohols of lower molecular weight are employed, e.g., butyl alcohol or lower, the phosphoryl derivative can be prepared best by reacting phosphorus oxychloride and the alcohol, and separating the pure alkyl phosphoryl dichloride by fractionation under reduced pressure. When higher molecular weight primary alcohols are used, a substantially pure alkyl phosphoryl dichloride is obtained directly from the reaction mixture of stoichiometric quantities of phosphorus oxychloride and alcohol. Secondary and tertiary alcohols do not give alkyl phosphoryl dichlorides under these reaction conditions. The reaction with sodium arylate is carried out in aqueous media. The products can be isolated and refined by customary techniques.

Only a few of the more useful and general preparative techniques have been described and actual preparative details have been omitted. Reference to the original literature and to survey books such as Kosolopoff's *Organophosphorus Compounds*³⁶ is recommended for more complete information.

PHYSICAL PROPERTIES

The physical properties of the tertiary phosphate esters are determined largely by the organic radicals attached to the phosphate moiety. Since many different types of organic groups can be present, properties of the esters can be varied considerably. In addition, certain properties of the phosphate esters are the direct result of the carbon-oxygen-phosphorus bonds. These properties are also greatly influenced by the organic groups. The variation of physical properties with both type and molecular weight of the organic portions of the phosphate esters is discussed in this section.

No attempt is made to include all the hundreds of tertiary phosphate esters reported in the literature. Many of the compounds are solids and are, therefore, of limited value as lubricants. The data generally reported on physical properties consist of density, boiling point, and refractive index with little, if any, information on properties required for evaluation as lubricants.

Again, the grouping into trialkyl, triaryl, and alkyl aryl phosphates is employed and comparisons are drawn between these groups.

PHYSICAL STATE

The tertiary phosphate esters vary in physical state from extremely mobile, low-boiling liquids to high-melting solids. The physical state is dependent upon the type of ester, its symmetry, and its molecular weight.

The trialkyl phosphates range from water-soluble liquids to essentially water immiscible liquids or low-melting solids as molecular weight is increased. Boiling points of some typical alkyl phosphates are given in Table 4.1.

TABLE 4.1. PHYSICAL PROPERTIES OF TRIALKYL PHOSPHATES.^{32, 33, 38}

Alkyl Group	Boiling Pt., °C/760 mm	Density 20°C/4°C	Viscosity, cp				
			20°C	25°C	30°C	35°C	40°C
Methyl	196	1.2144	2.26	2.03	1.82	1.66	1.52
Ethyl	215	1.0695	1.68	1.55	1.42	1.30	1.21
n-Propyl	252	1.0121	2.83	2.51	2.25	2.03	1.84
iso-Propyl	—	0.9867	—	—	—	—	—
n-Butyl	289	0.9766	3.89	3.42	3.02	2.70	2.44
iso-Butyl	264	0.9681	—	—	—	—	—
n-Amyl	—	0.9608	—	—	—	—	—

The triaryl phosphates, in contrast to the trialkyl phosphates, are much more viscous, have shorter liquid ranges, are essentially water-insoluble and in many cases are solids. Triphenyl phosphate, the first member of the series is a white solid melting at about 120°F. The addition of alkyl side chains on the aryl groups lowers the melting point to a minimum and then raises it again. Thus, increasing molecular weight results in the change—solid to liquid to viscous oil to solid.

The properties of the alkyl aryl phosphates are intermediate between those of the trialkyl and the triaryl phosphates. These compounds range from very mobile liquids to low melting solids. The physical state is quite dependent upon the exact chemical structure of the organic radicals making up the alkyl aryl phosphate.

DENSITY AND SPECIFIC GRAVITY

The weight-volume relationships of a lubricant are of importance in determining the flow characteristics and the weight of fluid required in the system. The phosphate esters are more dense than hydrocarbons of equivalent molecular weight.

The density or specific gravity of the trialkyl phosphates decreases as the length of the alkyl group increases. Data on typical compounds are given in Tables 4.1 and 4.2. It should be pointed out that branching of the alkyl groups results in decreased density. The effects observed are as would be predicted from the per cent carbon and hydrogen in the molecule and from a consideration of paraffin hydrocarbon densities.

The triaryl phosphates are more dense than the trialkyl phosphates. Specific gravity or density of typical triaryl phosphates is presented in Table 4.3. Alkylation of the aromatic rings results in decreased specific gravity. Condensed rings also usually result in increased specific gravity, as does chlorine substitution on the aromatic nucleus.

Specific gravity of the alkyl diaryl phosphates varies from a low of about 1.0 to a high of about 1.25. As illustrated in Table 4.4, the specific gravity is mainly a function of molecular weight.³³ An increase in molecular weight of the ester, whether caused by a change in the alkyl or aryl portion of the molecule, results in a decrease in specific gravity. Some variation in specific gravity is found between esters of the same molecular weight but of different structure. The effects of substituents on both the alkyl or aryl portions of the molecule are illustrated in Table 4.5.³⁵ Similar effects are found in the dialkyl aryl phosphate series.

Stepwise replacement of alkyl groups by aryl groups in the tertiary phosphate esters results in increased specific gravity as shown in Table 4.6.³⁵

VISCOSITY CHARACTERISTICS

Viscosity is one of the important properties in determining the suitability of a liquid for use as a lubricant. The variation of viscosity with tem-

TABLE 4.2. PHYSICAL PROPERTIES OF TRIALKYL PHOSPHATES.^{72, 74}

Alkyl Group	Sp. Gr. 25/25°C	Viscosity, cs			Viscosity Index	Pour Point, °F
		210°F	100°F	-40°F		
n-Butyl	—	1.09	2.68	47	118	-65
n-Hexyl	0.937	1.79	4.83	—	—	-70
2-Ethylhexyl	0.926	2.23	7.98	840	94	-65
n-Octyl	0.915	2.56	8.48	—	148	-30
n-Decyl	0.901	3.49	13.30	—	—	+20
Butoxyethyl	—	2.13	7.12	565	109	-65
2-Chloroethyl	—	3.75	21.58	17,230	43	-65

TABLE 4.3. PHYSICAL PROPERTIES OF TRIARYL PHOSPHATES.^{72, 74}

Aryl Groups	Sp. Gr. 25/25°C	Pour Point °C	Viscosity, cs		ASTM Slope 210-100
			210°F	100°F	
Cresyl diphenyl	1.205	-30	8.25	17.53	28
Dicresyl phenyl	1.180	-20	3.79	24.9	-
Tricresyl ^a	1.161	-15	4.37	35.11	0.886
Tri(2,4-dimethyl phenyl)	-	-	7.71	201.3	1.014
Tri(3,5-dimethyl phenyl)	-	-	6.39	94.1	1.009
Tri(meta-isopropyl)	-	-	5.53	42.72	59
Tri(para-isopropyl)	-	-	6.14	53.60	50
Tri(<i>p</i> -tert. butyl- phenyl)	-	-	15.43	750	0.955
Tri(<i>o</i> -chlorophenyl)	1.408 ^b	+5	5.95	65.3	0.883
1-Naphthyl diphenyl	1.247 ^b	128°	5.94	-	-
2-Naphthyl diphenyl	1.240 ^b	148°	5.58	-	-
3-Pyridyl diphenyl	-	91°	3.38	18.9	0.881

atypical commercial product

^b 25°C

40°C

melting point

perature as well as actual viscosity must be considered. A convenient measure of this characteristic is the viscosity index (ASTM D 567-53) or V.I.,² which relates the viscosity of the fluid at 210° and 100° F to that of a series of mineral oils. The larger the number the less change in viscosity with temperature.

TABLE 4.4. SPECIFIC GRAVITY AND POUR POINT OF ALKYL DIARYL PHOSPHATES.³³

Phosphate Ester	Molecular Weight	Sp. Gr. 25/25°C	Pour Point, °F
Methyl diphenyl phosphate	264	1.231	Below -70
n-Butyl diphenyl phosphate	306	1.151	Below -70
2-Ethylbutyl diphenyl phosphate	334	1.122	Below -70
2-Ethylbutyl dicresyl phosphate	362	1.088	-55
n-Octyl diphenyl phosphate	362	1.086	Below -70
2-Ethylhexyl diphenyl phosphate	362	1.090	Below -70
n-Octyl dicresyl phosphate	390	1.060	-60
2-Ethylhexyl dicresyl phosphate	390	1.063	-55
n-Dodecyl diphenyl phosphate	418	1.040	-10
Tetradecyl (branched) diphenyl phosphate	446	1.038	-40
n-Hexadecyl diphenyl phosphate	474	1.012	+45

TABLE 4.5. PHYSICAL PROPERTIES OF ALKYL DIARYL PHOSPHATES.⁸⁵

Phosphate Ester	Sp. Gr. 25/25°C	Viscosity, cs		Pour Point °F
		210°F	100°F	
Butoxyethyl diphenyl	1.145	2.56	10.66	-70
Butoxyethyl di(<i>o</i> -chlorophenyl)	1.237	-	-	-
Benzoxymethyl diphenyl	1.209	-	-	-
2-Chloroethyl diphenyl	1.278	2.71	12.94	27
2-Ethylhexyl phenyl	1.077	2.78	12.80	49
Di(isopropylphenyl)	1.033	3.85	22.4	46
2-ethylhexyl	-	-	-	-
Di(α -naphthyl) 6-methylheptyl	1.155	18.4	557.2	+10
Di(β -naphthyl) 2-ethylhexyl	1.142	9.26	167.3	-
Di(<i>o</i> -methoxyphenyl) 2-ethylhexyl	1.134	6.26	84.9	-
Di(<i>o</i> -chlorophenyl) 2-ethylhexyl	1.205	-	-	-
Di(<i>o</i> -nitrophenyl) 2-ethylhexyl	1.236	7.32	82.2	27

The viscosity index has certain deficiencies and many other methods have been proposed to rate viscosity-temperature characteristics in terms of a single number. An excellent review of this subject is given by E. E. Klaus.⁴⁵ In this chapter both V.I. and ASTM slope are used. The ASTM slope is defined as the slope of the curve of viscosity vs temperature plotted on standard ASTM paper (ASTM D 341-43).³

TABLE 4.6. EFFECT OF STEPWISE REPLACEMENT OF ALKYL GROUPS BY ARYL GROUPS.³⁶

Phosphate Ester	Sp. Gr. 25/25°C	Viscosity, cs			Pour Point °F
		210°F	100°F	-40°F	
Tri(2-ethylhexyl)	0.926	2.23	7.98	840	94
Di(2-ethylhexyl) phenyl	0.990	2.25	8.66	1840	67
2-Ethylhexyl diphenyl	1.090	2.45	10.01	5800	65
Triphenyl	-	-	-	-	122 ^a
Tri(n-octyl)	0.915	2.56	8.48	-	148
Di(n-octyl) cresyl	0.980	2.63	9.99	8910	108
n-Octyl dicresyl	1.060	3.15	15.30	-	61
Tricresyl	1.161	4.37	35.11	-	-15

^a melting point

Viscosity and viscosity-temperature properties are greatly affected by the chemical structure of the phosphate ester. These factors are discussed for each group.

Trialkyl Phosphate Esters. In the trialkyl phosphate esters, viscosity increases with increase in molecular weight as shown in Tables 4.1 and 4.2. As is often the case, the methyl derivative does not fit this generality. The straight-chain trialkyl phosphates are more viscous than the branched-chain isomers as shown in Tables 4.2 and 4.7. On the other hand, the normal isomers have the higher V.I. Chlorine substitution in the alkyl group greatly increases viscosity while the ether groups in the chain have comparatively little effect.

TABLE 4.7. TRIALKYL PHOSPHATE VISCOSITY.⁵⁰

Alkyl Group	Viscosity, cps						
	140°F	68°F	32°F	-40°F	-22°F	-40°F	-58°F
n-Hexyl	3.5	11.9	28	117	285	780	2000
2-Ethylbutyl	2.9	8.6	16.8	43	84	234	850

Triaryl Phosphate Esters. The triaryl phosphates have greater viscosities and inferior viscosity-temperature characteristics compared to the trialkyl phosphates of equivalent molecular weight. Alkylation of the aryl group generally results in increased viscosity and decreased V.I. or increased ASTM slope as shown in Table 4.3. Negative V.I.'s are not valid and, therefore, ASTM slopes are used. A decrease in slope means less change in viscosity with change in temperature. High-temperature viscosity data for several triaryl phosphates have been determined by Klaus and Fenske^{42, 43} and are given in Table 4.8.

Alkyl Aryl Phosphate Esters. Alkyl aryl phosphates are known having viscosities ranging from 1.5 to 10 centistokes at 210°F with V.I.'s as high as 160.³⁵ The viscosity of these esters is greatly influenced by the structure

TABLE 4.8. HIGH TEMPERATURE VISCOSITY OF TRIARYL PHOSPHATES.

Phosphate Ester	Viscosity, cps						
	100°F	180°F	210°F	490°F	707°F		
Tris(<i>o</i> -chlorophenyl) phosphate	—	23.4	5.65	0.87	0.45		
Phenyl <i>o</i> -chlorophenyl phosphate (1:1)	—	—	4.34	0.76	0.41		
Tris(chlorophenyl) phosphate (1:1 <i>ortho</i> :meta)	—	15.9	4.38	0.75	0.41		
Trioresyl phosphate	38.3	—	4.48	0.80	—		

of the substituent groups as well as by molecular weight. These variations in viscosity are illustrated by the data of Table 4.9.³⁵

It can be seen that an increase in the number of carbon atoms in the alkyl groups results in increased viscosity for those esters greater in molecular weight than butyl diphenyl phosphate. This compound has the lowest viscosity at -40°F of all the alkyl diaryl phosphates studied. Low-temperature viscosities cannot be measured for the higher alkyl diphenyl phosphates since they are solid at -40°F. In general, the V.I. is in the same range for all the branched-chain alkyl diphenyl phosphates but increases with molecular weight for the straight-chain alkyl diphenyl phosphates.

Viscosity of the alkyl diaryl phosphate series varies with molecular weight and also with differences in the structure of the alkyl group. Examples of this are given in Table 4.9. At low temperatures (-40°F) the

TABLE 4.9. VISCOSITY OF ALKYL DIPHENYL PHOSPHATES.³⁵

Alkyl Group	Viscosity, cps			Viscosity Index
	210°F	100°F	-40°F	
Methyl	2.15	8.32	5500	54
n-Propyl	2.06	7.67	2400	60
n-Butyl	2.02	7.30	1700	67
2-Methylpropyl	2.16	8.53	6000	47
n-Pentyl	2.19	8.26	2400	69
n-Hexyl	2.23	8.36	2400	76
2-Ethylbutyl	2.25	8.71	4200	65
n-Octyl	2.51	9.73	2200	90
2-Ethylhexyl	2.45	10.01	5800	65
6-Methylheptyl	2.61	10.87	7300	73
n-Decyl	2.87	11.54	3100	107
2-Butylhexyl	2.79	12.37	—	65
n-Dodecyl	3.24	13.76	—	117
Tetradecyl	3.97	22.19	—	69
n-Hexadecyl	4.70	20.70	—	162

n-alkyl diphenyl phosphate is much less viscous than the branched-chain isomer. No such clear-cut relation holds for higher temperatures as either isomer may have the higher viscosity.

The structure of the aryl group is also of importance in establishing the viscosity of the alkyl aryl phosphates. Representative examples are given in Table 4.10.³⁵ The replacement of phenyl groups by other aryl groups results in an increase in viscosity and a decrease in viscosity index.

To summarize the influence of structure of the alkyl diaryl phosphate upon viscosity, it can be said that increased molecular weight causes in-

TABLE 4.10. VISCOSITY OF ALKYL ARYL PHOSPHATES.³⁵

Phosphate Ester	Viscosity, cs		Viscosity Index
	210°F	100°F	
2-Ethylbutyl diphenyl phosphate	2.25	8.71	65
2-Ethylbutyl dioctyl phosphate	2.85	14.02	29
2-Ethylhexyl diphenyl phosphate	2.45	10.01	65
2-Ethylhexyl phenyl cresyl phosphate	2.78	12.80	49
2-Ethylhexyl dioctyl phosphate	3.17	16.94	25
2-Ethylhexyl di(methoxyphenyl) phosphate	6.26	84.9	—
2-Ethylhexyl di(β-naphthyl) phosphate	9.26	167.3	—
2-Ethylhexyl diphenyl phosphate	3.00	13.52	77
2-Butyloctyl diphenyl phosphate	3.76	21.78	41

creased viscosity, a change from straight- to branched-chain alkyl groups results in lower viscosity index, and increased complexity of the aryl groups leads to increased viscosity and decreased viscosity index. Somewhat similar results have been observed for the dialkyl aryl phosphates.

The effects on viscosity of stepwise replacement of alkyl groups by aryl groups in the tertiary phosphate esters are illustrated in Table 4.6. Such replacement results in increased viscosity at all temperatures and decreased viscosity index. Although this is exactly true for those compounds consisting of eight-carbon alkyl groups and phenyl or cresyl aryl groups, the use of other substituents may result in reversals of these properties. However, the general trends indicated have been observed in many series of phosphate esters.

LOW TEMPERATURE PROPERTIES

In many uses of synthetic lubricants the low temperature characteristics are important. Low temperature properties can be measured by pour points (ASTM D 97-57)⁴ or by viscosity at low temperatures.

Certain of the phosphate esters are crystalline solids at room temperature or slightly below. Crystallizing and melting points together with viscosity are better measures of low temperature capabilities.

The pour points of trialkyl phosphates increase with increasing length of the alkyl group, as shown in Table 4.2. Straight-chain trialkyl phosphates have higher pour points than the branched-chain isomer. Viscosity data at the lower temperatures demonstrate these same conclusions, as shown in Tables 4.2 and 4.7.

The triaryl phosphate esters, in general, have poor low-temperature characteristics. Pour points are seldom much below -30°F, as shown in Table 4.3. These points range upward until the phosphate esters become solid glasses at room temperature. The simplest triaryl phosphate, tri-

phenyl phosphate, is a crystalline solid melting about 120°F. Triaryl phosphates containing a mixture of aryl groups have better low-temperature properties than the completely symmetrical compounds.

The pour points of some alkyl diaryl phosphates are given in Tables 4.4 and 4.5. In general, the alkyl diaryl phosphates of lower molecular weights than the examples given, and also most of the dialkyl aryl phosphates, have pour points below -70°F. In the alkyl diaryl phosphate series, the pour point increases with an increase in chain length of the alkyl group, with the straight-chain isomer having a higher pour point than the branched isomer. The alkyl dioctyl phosphates have lower pour points than the corresponding alkyl diphenyl phosphates. The viscosity data shown in Table 4.9 further illustrate these conclusions.

In summary, the symmetry of the phosphate esters influences physical state and viscosity characteristics. Decreasing symmetry by alkylation of aryl groups or by branching of alkyl groups generally raises the pour point or melting point, decreases the viscosity index and increases the viscosity.

HEAT TRANSFER CHARACTERISTICS

Heat transfer characteristics are important in the synthetic lubricant field because one of the most important functions of a lubricant is to remove heat. Therefore, values for specific heat and thermal conductivity are useful to design engineers for determining heat transfer properties which will influence flow rates, the amount of cooling required, and certain mechanical characteristics of the system.

A reliable and easy-to-use method has recently been developed for the determination of thermal conductivity.²¹ The data obtained for several phosphate esters, along with some specific heat data, are given in Table 4.11.

TABLE 4.11. HEAT TRANSFER CHARACTERISTICS.^{10,24}

Phosphate Ester	Thermal Conductivity K X 10 ⁵ (Cal/cm °C sec)			Specific Heat 100°C
	28°C	81°C	82.5°C	
2-Ethylhexyl diphenyl	31.3	30.0	0.42	0.46
Isocetyl diphenyl	30.0	30.7	—	—
Tri(2-ethylhexyl)	31.2	28.5	—	—
Tricresyl	31.7	31.1	0.47 ^a	—

^a Room Temperature

VOLATILITY

Volatility is an important characteristic in determining the usefulness of a material as a synthetic lubricant. Although the volatility of the phos-

phate esters varies widely, it is sufficiently low within the usable temperature ranges that little difficulty exists in using the esters at ordinary pressures.

The lower trialkyl phosphate esters are relatively low boiling liquids, the triaryl phosphate esters are high boiling liquids or solids. The vapor pressure of the tertiary phosphate esters is directly related to molecular weight in any particular series, decreasing as molecular weight increases.

Recent work²⁸ on the vapor pressure of various phosphate esters has developed the constants for the vapor-pressure equation:

$$\log P (\text{mm of Hg}) = -A/T + C$$

The constants for this equation for various phosphate esters are given in Table 4.12.

TABLE 4.12. VAPOR PRESSURE OF PHOSPHATE ESTERS.²⁹

Phosphate Ester	A	C	Heat of Vaporization Kcal/mole
Triphenyl	4253	9.07	19.5
Tri- <i>m</i> -tolyl	5787	11.55	26.5
Tri- <i>o</i> -tolyl	4535	9.44	20.7
<i>p</i> -tert. Butylphenyl diphenyl	4444	9.24	20.3
Bis(<i>p</i> -tert. butylphenyl) phenyl	4896	9.59	22.4
<i>o</i> -Chlorophenyl diphenyl	4114	8.73	18.8
Bis(<i>o</i> -chlorophenyl) phenyl	4590	9.31	21.0
Tolyl diphenyl	3448	7.29	15.8
Butyl diphenyl	1582	4.12	7.2
Dibutyl phenyl	1921	4.99	8.8
Tris (2-chloroethyl)	1917	5.22	8.8
2-Ethylhexyl butyl phenyl	2634	6.13	11.8
Bis (2-ethylhexyl) phenyl	3417	8.16	15.9

TOXICITY

The toxicity of the phosphate esters is quite variable and ranges from completely innocuous and approved for use in food wrappings to extremely poisonous. The toxicity of each specific ester must be determined before approval is given for widespread adoption of the material. Detailed discussions of toxicity of each specific phosphate ester is beyond the scope of this chapter. Suppliers of phosphate esters and formulations containing such materials can furnish specific toxicological data and should be contacted to determine handling and operating precautions.

PERFORMANCE PROPERTIES

FIRE RESISTANCE

One of the outstanding characteristics of the phosphate esters is their ability to resist ignition. Many uses of phosphate esters depend upon this particular property.

The measurement of fire resistance of fluids and lubricants is extremely complex and there is no single test that can be used to evaluate all types of materials. The degree of fire resistance in a given test is influenced by the characteristics of the compound under test, by the type of flame or source of ignition being used, by the total amount of energy in relation to the amount of fluid, by the physical state of the fluid, and by many other factors.

The determination of fire resistance has been the subject of considerable research. Part of this research has been directed toward fundamental mechanisms of combustion. However, most of the effort has involved the development of test procedures which attempt to simulate actual ignition hazards in a uniform and reproducible manner.

Extensive work has been done regarding fire hazards of aircraft hydraulic systems. A group in the Society of Automotive Engineers studied this problem and developed a flammability specification,¹ AMS-3150B, for fire-resistant aircraft hydraulic fluids. This specification defines fire resistance in terms of performance of a standard fluid in a series of tests. The Air Force later set up a target specification for fire-resistant aircraft hydraulic fluids, MIL-F-7100.⁶⁴ These two specifications include the same general types of fire-resistance tests. These tests were designed to simulate conditions in aircraft resulting from a broken line spraying hydraulic fluid into a source of ignition, such as a flame or a hot surface. The names of these tests are "High Pressure Spray Test," "Low Pressure Spray Test" and "Hot Manifold Test." In addition, the military specification includes a test involving ignition of the fluid by incendiary gunfire. These tests have been used by many experimenters to study the fire resistance of fluids and lubricants including the phosphate esters.

In addition to the foregoing tests, other types of spray flammability tests have been designed and used to evaluate the phosphate esters. Thus, oxygen concentration required to sustain ignition has been proposed as a measure of fire resistance. Many other tests designed to evaluate fluids under a specific set of conditions have been formulated and used. No attempt will be made to review completely all types of flammability tests that have been proposed or used with the phosphate esters.

Since standard procedures for determining fire resistance and relating test data to actual use were not available, a committee was established by the American Society of Testing Materials (ASTM) to consider these prob-

lems. The group operates as Section VI of Technical Committee N on Hydraulic Fluids under ASTM Committee D-2. This section is attempting to correlate current flammability tests, to standardize the test conditions and to develop new test procedures. Early studies indicated that both simple laboratory procedures and larger scale simulative procedures were desirable. A series of round-robin tests was undertaken and will continue until reproducible and meaningful procedures are developed. The phosphate esters are one of the types of fluids under study in these investigations. The work of this committee should result in a better understanding of the phenomena of fire resistance and in the development of standardized flammability tests.

Flash and fire points are often used to measure the flammability of petroleum oils (ASTM D92-57).⁶ However, under the temperature and heating conditions of this test, the phosphate esters decompose to give flammable products which then burn. The temperature at which this occurs has little relationship to the actual temperature conditions under which the phosphate esters are fire resistant when tested using various spray and mist-forming techniques.

The phosphate esters have flash points which range from about 200 to 500° F, which are not much higher than those for petroleum oils of comparable volatility. These flash points are not generally considered to be a true measure of fire resistance but are more a measure of volatility and thermal stability.

The fire points of the phosphate esters are from 50° to as much as 300° F above the flash point. Again, these fire points are generally not considered true measures of phosphate ester flammability characteristics since, at the temperatures involved, many of these esters are thermally unstable.

The spontaneous or autogenous ignition temperature is a better measure of the flammability characteristics of the phosphate esters. This test involves placing a small amount of material on a heated surface and determining the temperature at which spontaneous ignition will occur (ASTM D286-587).⁶ The spontaneous ignition temperatures of the phosphate esters range from about 800° to above 1100° F.

Mecklenborg¹⁰ has studied the spontaneous ignition temperatures of a series of organic compounds. He found that the temperature correlates with ease of oxidative attack on the hydrogen in the alkyl group. Phosphate esters generally follow this pattern except for a decrease in ignition tendency in passing from triethyl to trioctyl phosphate.

In general, an increase in the carbon-to-phosphorus ratio in the phosphate esters results in a decrease in spontaneous ignition temperature. Furthermore, the aryl-containing phosphate esters have higher spontaneous ignition temperatures than the alkyl-containing phosphate esters of equivalent volatility.

Recently, much interest has arisen in the compression ignition characteristics of the phosphate esters. It has been found that air under high pressure suddenly expanding into a confined space coated with organic matter can cause ignition and explosion depending on rate of pressure release, volume of air flow, and quantity of fluid. An article by King and Coyle⁴ of the Bureau of Ships, U.S. Navy, describes some tests used to study the compression ignition of various fluids. In these tests, the phosphate esters showed greatly improved fire-resistance characteristics as compared to petroleum oils.

Many studies have been conducted by different investigators on the flammability of specific phosphate esters; the resulting data are readily available in the literature. In summary, the phosphate esters exhibit a high degree of fire resistance in most of these tests. The phosphate esters are not to be considered nonflammable. They will burn if the source of energy is sufficiently large and if the physical conditions are favorable. However, the tertiary phosphate esters do possess significant fire-resistance characteristics and are of practical value in many hazardous applications.

LUBRICATION CHARACTERISTICS

The primary function of a lubricant is to reduce the friction between two contacting surfaces. Secondary functions such as removal of heat, sealing out undesirable substances, and carrying additives to the surface are also important. The type of lubrication depends largely upon the thickness of the lubricating film. Two fundamental types are usually recognized—hydrodynamic (thick film) and boundary (thin film).

In the area of hydrodynamic lubrication, the most important characteristic of the lubricant is its viscosity. Since the tertiary phosphate esters have viscosities ranging from very low to very high, a phosphate ester can be selected which will operate satisfactorily as a lubricant under strictly hydrodynamic conditions. Certain phosphate esters have good viscosity-temperature characteristics although in general these characteristics are not so good as those of many other classes of synthetic lubricants. However, the alkyl-containing phosphate esters do have viscosity-temperature properties equivalent to petroleum oils while the triaryl phosphates have poorer viscosity-temperature properties. In many cases, the conditions of use are such that high viscosity index is not required. Where this situation exists the aryl phosphate esters perform satisfactorily and may be preferred because of stability or other properties.

Viscosity becomes much less important in the area of boundary lubrication and the chemical characteristics of the lubricant determine its lubricating ability. A number of studies have been carried out using various types of phosphorus compounds as the lubricant or as a lubricant additive. Many of these involve the use of substituted phosphoric acids,

i.e., the primary and secondary phosphate esters. These compounds have been shown to be very active anti-wear additives. Effectiveness is greatly improved if some sulfur is combined in the molecule. Thus, the thiophosphates and dithiophosphates are widely used as additives to improve the lubricating characteristics of many types of fluids. The tertiary phosphate esters are also effective lubricating additives.

The phosphate esters and, in fact, phosphorus compounds in general are in the class of anti-wear or chemical polishing agents. Klaus and Fenske⁴⁴ state that: "Phosphorus-containing lubricity additives, e.g., tri-cresyl phosphate, appear to function by means of a chemical polishing mechanism. Most other lubricity additives, including fatty acids and typical sulfur chlorine extreme-pressure additives, function as chemically erosive materials at the bearing surfaces." According to this chemical polishing mechanism, a local "hot-spot," caused by friction, results in the reaction of the additive with the metal to form a lower melting alloy which is deformed by plastic flow to allow a new distribution of the load.

The work of Beeck¹¹ supports this mechanism for excellent lubricity of tertiary phosphate esters used as the sole lubricant. He suggests that these esters function as lubricants by reacting with the metal surface to form metal phosphides. The phosphide films produced on the high spots of the bearing surfaces are low-melting eutectics. These films are wiped into the depressions between the high spots to increase the actual bearing contact area and reduce bearing pressure. Beeck and co-workers¹⁰ found that tricresyl phosphate is effective only on steel or other metals capable of reacting with tricresyl phosphate to form a lower melting alloy. On gold and tungsten, for example, tricresyl phosphate is ineffective.

Two further studies of lubrication with phosphate esters are of interest. The first by Borsoff¹³ concerns tri(2-ethylhexyl)phosphate as a gear lubricant using radioactive gears. The type of wear found was gear scoring as would be predicted from the mechanism of chemical polishing.

The second study was carried out by workers at the New York Naval Shipyard concerning the fatigue life of heavily loaded angular contact ball bearings.²⁰ The series of lubricants used included a petroleum oil as a standard, an aryl phosphate ester fluid, a fire-resistant fluid containing a phosphate ester as part of its base stock, and a water-glycol type fluid. The fatigue life of these bearings using the phosphate ester was 58 per cent of that using the petroleum oil. The other fluid containing some phosphate ester gave somewhat greater reduction in the life of the bearing. No satisfactory explanation has been developed for the reduction in the life of ball bearings under the particular conditions used in this study, nor has correlation with service life under actual operating conditions been determined.

Many other studies affirm the excellent lubricating characteristics of

the phosphate esters. Actual service experience has demonstrated increased life of pumps, bearings, and machinery operating on phosphate ester fluids. It is, therefore, apparent that bench-scale test results concerning lubricating characteristics must be carefully interpreted in terms of actual use conditions.

In conclusion, the tertiary phosphate esters should be classed as excellent lubricants. Use of these esters under conditions which conform to the limits set by other properties will not result in failure due to poor lubricity.

HYDROLYTIC STABILITY

The resistance of a material to degradation by water can be an important characteristic in its use as a lubricant. Obviously, the degree of resistance required will vary with the specific application.

Since the phosphate esters can be considered as the reaction products of an organic alcohol or phenol and an inorganic acid (phosphoric), the reaction could be reversed by water. Therefore, the phosphate esters must have some degree of hydrolytic stability, i.e., resistance to attack by water. The hydrolytic stability is very dependent upon the structure and the molecular weight of the phosphate ester.

A study of hydrolytic stability as it relates to chemical structure of phosphate esters was conducted by Gamrath, Hatton, and Weesner.³⁵ Data were obtained by refluxing a weighed sample of the ester with freshly boiled distilled water for a definite time and then measuring the total acidity of both water and oil layers. Detailed results of this study are recorded in Table 4.13.

Several conclusions may be drawn concerning the effect of structure on the hydrolytic stability of the alkyl diaryl phosphates. In general, an increase in the molecular weight of the alkyl group increases the resistance to hydrolysis. The alkyl ditolyl phosphates are more hydrolytically stable than the corresponding alkyl diphenyl phosphates. In a series of isomeric alkyl diaryl phosphates, the *n*-alkyl isomer is less hydrolytically stable than the branched-chain isomer. In the study by Gamrath *et al.*, the maximum resistance to hydrolysis was found in the ester where the alkyl part of the molecule had both hydrogens on the number two carbon replaced by methyl groups. This blocking effect of groups larger than hydrogen atoms was also observed in a study of the hydrolytic stability of alkyl esters of dibasic acids.¹⁴

The alkyl aryl phosphates are slightly less hydrolytically stable than the trialkyl and triaryl esters, although, as can be seen from Table 4.13, individual members have stabilities equivalent to both comparative classes.

Grafstein³⁹ studied the hydrolytic stability of the aryl phosphate esters. He found that aromatic phosphate esters are not hydrolytically stable at

TABLE 4.13. HYDROLYTIC STABILITY OF PHOSPHATE ESTERS.³⁶
(24-Hour Reflux Period)

Phosphate Ester	MI IN NaOH/Mole
<i>n</i> -Butyl diphenyl	27.8
2-Methylpropyl diphenyl	7.3
<i>n</i> -Pentyl diphenyl	19.7
3-Methylbutyl diphenyl	8.5
2-Methylbutyl diphenyl	15.4
2,2-Dimethylpropyl diphenyl	1.6
<i>n</i> -Hexyl diphenyl	16.5
2-Methylpentyl diphenyl	2.7
2-Ethylbutyl diphenyl	4.8
<i>n</i> -Octyl diphenyl	14.6
6-Methylheptyl diphenyl	7.6
2-Ethylhexyl diphenyl	3.6
<i>n</i> -Decyl diphenyl	8.2
2-Ethylloctyl diphenyl	7.0
<i>n</i> -Dodecyl diphenyl	6.5
2-Butyloctyl diphenyl	4.0
<i>n</i> -Hexyl ditolyl	4.5
2-Ethylbutyl ditolyl	2.3
<i>n</i> -Octyl ditolyl	4.4
2-Ethylhexyl ditolyl	1.7
<i>n</i> -Decyl ditolyl	3.3
2-Ethylloctyl ditolyl	2.9
<i>n</i> -Dodecyl ditolyl	3.5
2-Butyloctyl ditolyl	2.2
Tri(<i>n</i> -butyl)	4.0
Tri(2-ethylhexyl)	0.2
Tritolyl	1.2

elevated temperatures. The point of hydrolytic breakdown is apparently the phosphorus-oxygen bond so that the products of hydrolysis include phenols as well as substituted phosphoric acids.

All esters will hydrolyze under certain conditions. As a class, the phosphate esters are poorer than the organic esters and better than the silicate and borate esters in hydrolytic stability. The resistance to hydrolysis is sufficient in nearly all cases to enable the phosphate esters to satisfactorily perform their lubricant functions.

THERMAL STABILITY

The temperature range over which a lubricant can be used is determined by its low temperature properties for the minimum temperature and by its thermal stability for the maximum temperature. Thermal stability is usually

measured in terms of temperature and time. The shorter the time the lubricant is exposed to heat, the higher the temperature that can be tolerated. The amount of decomposition that can be permitted is determined by the specific application.

Thermal stability of the phosphate esters is dependent upon chemical structure. The mode of decomposition is different for each group and differs even for different structures within each group. The triaryl phosphates are considerably more thermally stable than the trialkyl phosphates.

In comparative studies on thermal stability, the decomposition temperature was found to be about 790° F for triphenyl phosphate and about 380° F for trioctyl phosphate.¹² The decomposition temperature is defined as the temperature at which the pressure rise is 0.014 mm Hg per second as determined in an isothermoscope. The test is run with the material under vacuum after flushing with nitrogen so that oxidative effects are eliminated. The decomposition temperature is not necessarily a temperature at which the material can be used, but serves as a method of rating comparative thermal stability.

Triaryl Phosphate Esters. In an Air Force-sponsored study of thermally stable materials, Raley⁷³ prepared a large number of triaryl phosphate esters which included naphthyl derivatives, biphenyl derivatives, and chlorinated phenyl derivatives. The chlorophenyl phosphates possessed outstanding thermal stability and were considered worthy of further study. Some of the compounds prepared had thermal stabilities as high as 950° F in Raley's tests. From his studies, a series of approximate thermal decomposition temperatures of aryl groups in phosphate esters was developed. A representative number of these are given in Table 4.14. It appears that alkyl substituents on the aryl group decrease thermal stability.

Later work by Dacons and Schiefer⁷⁵ confirmed that the chlorophenyl phosphates were thermally stable, but were not stable in the presence of iron or other metals. It is apparent that the chlorine-containing group weakened the stability of the compound through metal attack.

TABLE 4.14. COMPARATIVE THERMAL DECOMPOSITION TEMPERATURES OF TRIARYL PHOSPHATE ESTERS.⁷³

Aryl Group	Decomposition Temperature, °F
Phenyl	> 905
<i>m</i> -Tolyl	705
<i>p</i> -Tolyl	740
<i>o</i> -Chlorophenyl	> 950
<i>m</i> -Chlorophenyl	> 870
<i>p</i> -Chlorophenyl	> 880
1-Naphthyl	890
2-Naphthyl	880

Klaus and Fenske⁴³ of the Petroleum Refining Laboratory at Pennsylvania State University studied tricresyl phosphate in their search for thermally stable fluids. Attempts to determine the viscosity of tricresyl phosphate at 707° F were unsuccessful because of decomposition. The stability of tricresyl phosphate was investigated by heating at 500 or 600° F in a glass tube. Under these conditions, significant decomposition was found to occur. Further tests carried out in a stainless-steel pressure cylinder at 600° F showed more decomposition than found in glass. The neutralization number reached 12.9 and the 100° F viscosity increased 33 per cent in six hours under these conditions. The corresponding data in glass for six hours were 2.8 increase in neutralization number and 8 per cent increase in 100° F viscosity.

The effects of oxidation in the presence of metals were studied at temperatures of 500° F. Test conditions included a test time of 24 hours, an air rate of 0.6 liters per hour, and a fluid charge of 100 ml. Under these conditions tricresyl phosphate showed an increase in viscosity of 232 per cent at 130° F and a neutralization number increase of about 40.

Klaus and Fenske concluded that tricresyl phosphate is usable as an additive at temperatures up to 500–600° F. The material itself, however, does not seem to be adequately stable at these temperatures for use as a fluid base stock or as a lubricant.

Further work with triaryl phosphates containing chlorine substituents on the phenyl ring resulted in conclusions similar to those cited above.⁴² These esters exhibited good thermal stability in glass systems at 700° F, but thermal stability at 600–700° F was materially reduced by the presence of metals such as copper, steel, and aluminum.

There is little reference in the literature to the mode of decomposition of the triaryl phosphates. However, it is known that substituted phosphoric acids are formed in the thermal decomposition of these materials and that these acids are corrosive to metals, particularly copper.

Practical considerations have indicated that for continuous use, temperatures must be limited to 300–350° F with the triaryl phosphates, but short-time exposure to higher temperatures can be tolerated.

Alkyl Diaryl Phosphate Esters. The neutral alkyl diaryl phosphate esters are very stable at room temperature. Samples have been stored for years without significant change in neutrality. However, at higher temperatures these esters are thermally unstable, the stability being dependent on time, temperature, structure and environment. The rate of decomposition is catalyzed by acids and can be inhibited by their removal or neutralization.

The thermal stability of the alkyl diaryl phosphate esters as a class was measured³⁶ by determining the loss in weight and the development of acidity in samples heated under controlled conditions.

In Table 4.15, comparative data on heat stability for certain of the alkyl diaryl, triaryl and triaryl phosphates are shown.

Several conclusions concerning the effects of structure can be drawn from these data. The alkyl ditolyl phosphates are more heat stable than the alkyl diphenyl phosphates. The straight-chain alkyl esters are more stable than the isomeric branched-chain alkyl esters. It also appears that the greater the amount of branching in the alkyl group, the less heat stable is the alkyl diaryl phosphate. For example, heat stability decreases in the series of *n*-hexyl, 2-methylpentyl, and 2-ethylbutyl diphenyl phosphates. The nearer the branching approaches the number one carbon position, the greater the instability of the ester, as exemplified by the decrease in stability of the *n*-octyl, 6-methylheptyl, and 2-ethylhexyl esters.

The decomposition of alkyl diaryl phosphates produces an unsaturated aliphatic hydrocarbon and a diaryl phosphoric acid.³⁶ Thus, 2-ethylhexyl diphenyl phosphate can be quantitatively decomposed on heating into 2-ethyl-1-hexene and diphenyl phosphoric acid.

It appears that in thermal decomposition the weakest point of the molecule is the oxygen-aliphatic carbon linkage. Other workers have confirmed this mode of decomposition. Noone⁷¹ recently reported that pyrolysis of cyclohexyl diphenyl phosphate at 356° F gives cyclohexene in 68 per cent yield and diphenyl phosphate in 90 per cent yield. It should be pointed out

TABLE 4.15. HEAT STABILITY OF ALKYL DIARYL PHOSPHATE ESTERS AT 302° F.

Phosphate Ester	(24-Hour Exposure)	
	Loss in Weight, %	1N NaOH/Mole ml
<i>n</i> -Butyl diphenyl	2.4	9
2-Methylpropyl diphenyl	2.8	11
<i>n</i> -Pentyl diphenyl	2.0	26
3-Methylbutyl diphenyl	3.2	28
2-Methylbutyl diphenyl	14.0	560
2,2-Dimethylpropyl diphenyl	—	3.5
<i>n</i> -Hexyl diphenyl	1.4	15
2-Methylpentyl diphenyl	2.4	28
2-Ethylbutyl diphenyl	3.0	76
<i>n</i> -Octyl diphenyl	0.8	31
6-Methylheptyl diphenyl	1.6	40
2-Ethylhexyl diphenyl	2.9	92
2-Ethylbutyl ditolyl	0.8	11
<i>n</i> -Octyl ditolyl	0.4	10
2-Ethylhexyl ditolyl	0.8	28
Tri(<i>n</i> -octyl)	3.2	12
Tri(2-ethylhexyl)	2.8	82
Triitolyl	0.4	3.5

that carboxylate esters decompose in a similar manner, giving an olefin and a carboxylic acid.

It is postulated that a hydrogen is necessary on the number two carbon atom for the formation of 1-alkene hydrocarbon and diaryl phosphoric acid. If both hydrogens on the number two carbon atom were replaced by alkyl groups, such as methyl groups, the resulting phosphate ester should be considerably more heat stable. The data for 2,2-dimethylpropyl diphenyl phosphate in Table 4.15 confirm this. The same effects have been noted for 2,2-dimethylbutyl diphenyl phosphate.

Practical consideration of utility vs temperature have indicated that alkyl aryl phosphates are satisfactory for continuous use at temperatures up to 225–250° F.

Trialkyl Phosphate Esters. The trialkyl phosphate esters decompose in a manner similar to that discussed for the alkyl aryl phosphates. The structural considerations outlined also apply to the trialkyl phosphates.

Baumgarten and Setterquist⁹ studied the decomposition of amyl dimethyl, dimethyl hexyl, dimethyl octyl, dioctyl methyl, and cyclohexyl dimethyl phosphate. These phosphate esters were pyrolyzed by passing them through a tube packed with glass helices at 660–930° F. Olefins were obtained in high yield in each instance. The pyrolyses were accompanied with extensive rearrangement of the olefinic double bond as would be expected using such temperatures.

In summary, the phosphate esters have a fair degree of thermal stability which is dependent upon the structure of the phosphate ester. In all cases, thermal decomposition forms substituted phosphoric acids which may be corrosive to metal. Thermal stability is a time-temperature function, the esters being more stable for longer times at lower temperatures. However, adequate thermal stability does exist for many applications.

OXIDATION STABILITY

The oxidation stability of phosphate esters is generally quite good. The data in the literature indicate that oxidation tests conducted at temperatures within the thermal stability limits of the particular phosphate ester show little, if any, change. At higher temperatures, both oxidative attack and thermal decomposition occur; it is difficult to separate the two effects. Data concerning the behavior of tricresyl phosphate under such conditions are given in the preceding section. Actual use of phosphate esters has not shown any real deficiencies because of oxidation instability.

CORROSION CHARACTERISTICS

The phosphate esters are generally not corrosive to most metals. Certain phosphate esters have been used for many years in steel systems with

no evidence of corrosion of any kind. Compatibility tests with many metals have shown that no problems should exist because of the corrosion characteristics of the phosphate esters. However, it is recommended that tests be conducted with the specific system metals under the expected operating conditions during the design phases of the development of new phosphate ester-containing mechanisms.

It should be pointed out that if breakdown does occur through thermal decomposition or hydrolytic attack the substituted phosphoric acids so formed are corrosive to certain metals, particularly copper. However, this is not necessarily true for copper-containing alloys.

Tertiary phosphate esters should not be considered as anti-rust materials. However, surfaces which have been covered with these esters do not rust as rapidly as those which have not been covered. It appears that tertiary phosphate ester is sufficiently strongly adsorbed to prevent moisture from coming in contact with the surface.

The primary and secondary phosphate esters neutralized with various nitrogen-containing compounds have been recommended as rust inhibitors and are used commercially in anti-rust formulations of mineral oil.

RADIATION RESISTANCE

Interest in recent years in the effects of various types of radiation on materials which are potential components of space vehicles, missiles, and nuclear reactors has led to extensive study of the interactions involved. Most work has been done at the request of or by military and government organizations. The tertiary phosphate esters are decomposed by most types of radiation. It is generally conceded that these materials lack sufficient radiation stability to be used as the primary lubricant for nuclear reactors or for equipment operating in high radiation environments.

One specific example from the literature concerns experiments with tributyl phosphate. Burger and McClenahan¹⁵ found that tributyl phosphate, under gamma radiation gave dibutyl phosphate, monobutyl phosphate, phosphoric acid, butanol, dibutyl ether, polymer, hydrogen and hydrocarbon. The principal product was dibutyl phosphate. Dilution of the phosphate with paraffin hydrocarbon did not change the yield, while dilution with benzene lowered the yield and dilution with carbon tetrachloride raised the yield. Saturation of the tributyl phosphate with water reduced the yield about thirty per cent.

Workers at the Shell Development Company¹⁶ have reported similar results. Tricresyl phosphate irradiated with gamma rays, after absorbing 10¹⁰ ergs per gram, formed large amounts of monobasic acid and increased about 50 per cent in viscosity. Similar results were obtained with aliphatic phosphate esters.

SOLVENT PROPERTIES

One outstanding property of the tertiary phosphate esters is their ability to dissolve many substances. They are good solvents for many organic materials such as hydrocarbons, alcohols, ethers, ketones, esters, etc. Certain nonpolar materials are not soluble in the tertiary phosphate esters.

The excellent solvent properties of the phosphate esters have caused some use problems. For example, esters may display incompatibility with certain materials normally used in lubrication systems or in the vicinity of such systems. These include elastomers, gaskets, seals, paints, wiring, fabrics, etc. However, it should be pointed out that these solvent effects are not universal and that materials have been developed which are satisfactory for use with the phosphate esters. For example, the tertiary phosphate esters swell and dissolve the Buna N type of synthetic rubber. However, Butyl-type synthetic rubber is satisfactory for use with the phosphate esters. A series of gaskets, packings and seals have been developed using the Butyl rubber elastomer so that satisfactory systems can be designed and used.

The phosphate esters are excellent plasticizers for the polyvinyl-type resins. On the other hand, highly crosslinked polymers such as epoxy, phenol-formaldehyde or thermosetting-type resins in general are resistant to attack by phosphate esters, as is nylon.

One additional solvent effect of the phosphate esters should be mentioned—they tend to remove dirt from new or used systems. The soluble portion remains in the liquid while insoluble contaminants are loosened and carried in suspension throughout the system. The use of filters is therefore recommended to remove the insoluble materials in any system using a phosphate ester as a circulating fluid. Filters which contain binders not affected by phosphate esters are required. The fluid should be examined to insure that soluble contaminants are not present in large enough amounts to cause system malfunction.

ADDITIVE SUSCEPTIBILITY

The addition of relatively small amounts of materials to improve the performance of a given fluid or lubricant is widely practiced with petroleum-derived products. In a similar manner, additives may be used with phosphate esters. The fact that the phosphate esters are good solvents makes formulation somewhat easier because a wide selection of potential additives is available. However, it should be noted that materials which perform certain additive functions in the hydrocarbon fluids may or may not perform the same function in the phosphate esters.

The literature records the use of viscosity index improvers, antirust agents, lubricity improvers, antifoamants, dyes, and other additives in the

phosphate esters. Furthermore, examples are given of lubricants prepared by blending various other synthetic or natural lubricants with the phosphate esters, again illustrating their good solvent characteristics.

SUMMARY OF PROPERTIES

The suitability of any class of material as a synthetic lubricant involves consideration of all properties as well as its performance characteristics. The preceding sections have been concerned with these characteristics of the phosphate esters. An over-all evaluation of the phosphate esters in comparison with petroleum-derived lubricants is now given.

The lubricating ability of the phosphate esters is well known and widely recognized. They have been used for many years as lubricity additives in petroleum and other synthetic lubricants. Many members possess sufficient stability to enable their use as the principal component of a synthetic lubricant.

The phosphate esters have excellent fire-resistant properties and are much better in this regard than equivalent viscosity petroleum oils. The oxidative stability of the phosphate esters is excellent, surpassing that of petroleum lubricants. Thermal stability, while satisfactory up to medium-high temperatures, is poor at high temperatures and the phosphate esters are not suitable for sustained high-temperature usage. Hydrolytic stability ranges from poor to very good depending on structure and molecular weight.

The volatility of the phosphate esters is quite low compared to petroleum hydrocarbons of similar viscosity. Viscosity covers an extremely broad range, including light mobile liquids to viscous oils. The viscosity-temperature characteristics of the phosphate esters can be classified as medium to good; i.e., they are the equivalent of average petroleum lubricants but do not approach the viscosity-temperature characteristics of the best petroleum products on an equivalent viscosity basis. Liquid range varies with molecular structure and weight but, in general, is quite wide.

The phosphate esters have excellent solvency properties and give miscible formulations with other synthetics, with many petroleum hydrocarbons, and with additives. They are strong solvents for many components of mechanical systems such as elastomers, gasket materials, surface coatings, wire coverings, plastics, fabrics, etc. However, such solvent effects are not universal and materials with satisfactory resistance to phosphate esters have been developed. Many additives are soluble in the phosphate esters and are effective in improving such characteristics as corrosion resistance, viscosity-temperature characteristics, rusting, foaming, etc.

Over-all, phosphate esters offer certain definite and important advan-

tages over petroleum hydrocarbons as lubricants. The major advantage is undoubtedly their fire resistance combined with their ability to lubricate moving parts, particularly steel-on-steel. The use of compatible system materials and the design of the actual operating system to conform to the characteristics of the phosphate esters have resulted in their widespread commercial utilization.

USES

GENERAL

The tertiary phosphate esters have found increasing commercial utility, especially in the past 10 to 15 years. New members of this class are being prepared and new uses are constantly being discovered. For many years, the tertiary phosphate esters have been incorporated in relatively small amounts as lubricating additives in petroleum-derived lubricants and, more recently, in diester and certain other synthetic-base lubricants. Tricresyl phosphate is the most widely used ester for these purposes.

Many members of the phosphate ester class possess sufficient chemical, thermal, and oxidative stability to enable their use as the principal ingredients of a synthetic lubricant. The excellent fire-resistance and lubricating characteristics of the phosphate esters are most important in determining their usefulness as functional fluids.

Fire-resistant hydraulic fluids represent the largest commercial use of tertiary phosphate esters in the field of synthetic fluids and lubricants.

There are many applications of hydraulic power in locations where ignition by various system or machine components is possible. For example, the hydraulic lines aboard aircraft often pass quite close to the engine exhaust system. A break in the line can allow the fluid to spray onto the hot metal parts. A flammable hydraulic fluid under such conditions may ignite and can result in burning and destruction of the aircraft. A fire-resistant fluid under similar conditions will prevent such fires.

Hazardous conditions also exist in industrial plants which use hydraulic power in various types of machinery. Operations which involve such hazards include die casting, metal handling, metal and plastic fabrication, heat treating, and the control of various mechanisms on or close to equipment operating at high temperatures. It is in these areas that fire-resistant fluids have found their principal application.

Lubricity, as well as fire resistance, is an important characteristic of hydraulic fluids. The primary function of the hydraulic fluid in a hydraulic system is to transmit energy from one location to another. The hydraulic pump, the valves, the motor, etc. contain parts which move in relation to each other. Hydraulic fluids with good lubricity are, therefore, required to

prevent metal-to-metal seizure and to reduce friction and wear. The phosphate esters are outstanding in this regard and have demonstrated their utility in many critical applications.

The tertiary phosphate esters are useful as components of fire-resistant air compressor or gas compressor lubricants. In addition, they are under study as steam turbine or gas turbine lubricants.

The phosphate esters are also used in low volatility, high lubricity greases, and as special low-temperature lubricants.

USES FROM THE PATENT LITERATURE

A review of the patent literature reveals many claims to the use of phosphate esters as synthetic lubricants, hydraulic fluids and major component in such products. Only those compositions containing at least ten per cent phosphate ester will be described. These patents will be discussed under the classifications previously used, i.e., the trialkyl phosphates, the alkyl aryl phosphates, and the triaryl phosphates. No attempt is made to list all such applications nor to include all proposed uses of phosphate esters claimed in the literature.

Trialkyl Phosphate Esters. Certain branched-chain trialkyl esters of phosphoric acid are said to be satisfactory synthetic lubricating fluids of low pour point and high viscosity index.⁵¹ The alkyl groups contain 8 to 20 carbon atoms each, may be alike or different and are obtained from products of the "Oxo" synthesis.

Phosphate esters of the formula $OP(ORXR')_3$, in which R is a saturated aliphatic hydrocarbon group having two or three carbon atoms, X is oxygen or sulfur and R' is an alkyl group containing one to eighteen carbon atoms or a series of saturated aliphatic hydrocarbon groups interlinked by oxygen or sulfur, are said to be effective lubricants for "prop-jet" engines and to improve the film strength and oiliness of mineral-oil blends.⁵² The compound $OP(OC_2H_5SC_8H_{17})_3$, in which C_8H_{17} is a tertiary octyl group is preferred.

Fluids consisting of triethyl phosphate and diisobutyl ketone are claimed as hydraulic fluids or de-icing fluids for aircraft.⁷⁶ The ketone inhibits corrosion.

Tributyl phosphate containing an extreme pressure agent such as tritolyl phosphite or chloromethyl stearate, a corrosion inhibitor such as lead naphthenate or oleate, and sulfurized tin alkylphenol carboxylate as corrosion inhibitor, antioxidant, and pour point depressant can be used in gun recoil piston cylinders and shock absorbers.⁴⁷ Other trialkyl phosphates are also suitable.

Trialkyl-Triaryl Phosphate Mixtures. Substantially fire-resistant lubricants and hydraulic fluids consisting of mixtures of a trialkyl phosphate and

a triaryl phosphate which may also contain viscosity index improvers, corrosion inhibitors, and antioxidants are claimed by Watson in two patents.^{90, 91} The triaryl phosphates, which comprise 50-90 per cent of the composition, contain alkyl groups of 4 to 9 carbon atoms with branched-chain alkyl groups being preferred. The triaryl phosphates have the general formula, $O:P(OR)_3$, in which one or two R's are phenyl radicals, and the remainder substituted phenyl radicals. Organic compounds containing an epoxy group such as glycidyl *o*-tolyl ether or organic sulfides or disulfides are used to inhibit corrosion and oxidation of metals by these phosphate ester fluids. A mixture of organic epoxy compounds with organic sulfides or disulfides is also claimed to decrease the corrosion of phosphate ester fluids according to a British patent.⁷

Another Watson patent claims hydraulic fluids useful at low temperatures and of low flammability consisting of trialkyl phosphates, triresyl phosphate, a linear polymer of methacrylic esters, and a glycidyl ether.⁹³ An example of such a composition contained 80 per cent tri (2-ethylhexyl) phosphate, 15 per cent tricresyl phosphate, 4 per cent Acryloid HF855 (a methacrylic ester polymer) and 1 per cent phenyl glycidyl ether. This composition had a viscosity index of 169, a pour point of $-65^{\circ}F$, and a flash point of $380^{\circ}F$.

A fire-resistant hydraulic fluid obtained by combining aryl phosphates containing three hydrocarbon groups with a trialkyl phosphate is described by Moreton.⁹⁵ Two of the three hydrocarbon radicals of the aryl phosphate are phenyl, tolyl, or xylol radicals, while the third is tolyl or xylol or a saturated alkyl radical of 6 to 10 carbon atoms. The alkyl groups in the trialkyl phosphate are saturated branched chains of 4 to 9 carbon atoms or saturated straight chains of 4 to 6 carbon atoms.

Solutions of thermoplastic water-insoluble resins made from substituted cellulose or polyvinyl or acrylic resins in trialkyl phosphates are said to be suitable hydraulic fluids or low-temperature lubricants because of their flat viscosity-temperature curve, low pour point, extreme-pressure lubricating characteristics, and low solvency for rubber.⁴⁰

Triaryl Phosphate Esters. Bearings such as those in gas meters can be lubricated without corrosion over long periods by the use of non-volatile esters of phosphoric acid, such as tricresyl phosphate.¹⁹

Air Force-sponsored work on the use of triaryl phosphate as high temperature lubricants resulted in a patent⁷⁶ on phenyl *m*-trifluoromethylphenyl l-naphthyl phosphate. This ester is said to have good stability and good lubricity. The patent describes several other examples of triaryl phosphates.

A French patent¹⁷ refers to the use of trixylol phosphate, alone or mixed with small amounts of oleic acid or olive oil, as lubricants.

An article by Egan⁸¹ details the properties of tricresyl phosphate and its use as a hydraulic fluid and lubricant additive.

Alkyl Aryl Phosphate Esters. A number of patents have been issued to the Douglas Aircraft Company concerning the formulation of alkyl aryl phosphates into fire-resistant fluids suggested for, but not specifically limited to, aircraft use. One of these⁶¹ covers fire-resistant hydraulic fluids which are also good lubricants, comprising a polyalkylmethacrylate and alkyl diaryl phosphate. The alkyl group of the polyalkylmethacrylate has 8 to 10 carbon atoms and the polymer has an average molecular weight of 8,000 to 12,000. The aryl groups of the phosphate ester consist of phenyl, tolyl and xylol radicals and the alkyl group is branched and contains 4 to 8 carbon atoms. A later patent extends the alkyl range of the phosphate ester from 4 to 10 carbon atoms.⁶²

Douglas Aircraft patents^{60, 63} also describe a fire-resistant hydraulic fluid consisting of a dialkyl phenyl phosphate and a polyalkylmethacrylate. The phosphate has 4 to 8 carbon atoms in each of the alkyl groups with a total of 8 to 12 carbon atoms in the two alkyl groups. The polyalkylmethacrylate increases the viscosity at elevated temperatures and also the viscosity index. The addition of a mixture of an epoxy compound and an alkylene diaryl sulfide in which the alkylene group has 1 or 2 carbon atoms and the aryl radicals have 6 or 7 carbon atoms is claimed to decrease the attack of this composition on copper.³⁰

Phosphate Ester-containing Mixtures. Many patents concern mixtures of trialkyl, triaryl, or alkyl aryl phosphates with other materials and their use as fluids and lubricants. Mixtures of phosphate esters and halogenated organic compounds as soluble one-phase synthetic lubricants are covered by a number of patents. These patents cover all types of phosphate esters and a wide variety of halogenated materials including chlorinated and fluorinated aliphatic and aromatic compounds.

Fluids useful as power transmission fluids and synthetic lubricants are obtained by mixing tricresyl phosphate, chlorinated biphenyl containing 40-60 per cent of combined chlorine, and small quantities of alkylated polystyrene.^{34, 37} Minor amounts of additives which may also be used in the products include antifoam, detergent and extreme pressure additives.

A Douglas Aircraft Company patent⁶⁸ relates to fire-resistant hydraulic fluids comprising triaryl phosphates or alkyl diaryl phosphates, and chlorinated biphenyls containing more than 40 per cent of combined chlorine. A minor proportion of an agent for increasing the viscosity index can be included.

Useful fluids and lubricants are said to result from mixing chlorinated biphenyls with the lower molecular weight alkyl phosphates, i.e., trialkyl phosphate of 4 or less carbon atoms such as triethyl or tributyl phos-

phate.^{22, 23} A patent by Caprio¹⁸ describes steam turbine lubricants prepared by mixing equal parts of chlorinated biphenyl and tricresyl phosphate. Polyesters or polyether-esters with oxygen atoms in the chain are said to be viscosity index improvers for hydraulic fluids based on mixtures of chlorinated hydrocarbons and phosphate esters.⁷⁰ Phosphate esters have been mixed with other halogenated materials to yield products claimed as fire-resistant hydraulic fluids.⁸ For example, products such as hexachlorobutadiene or hexabromopropene, can be used with trialkyl or triaryl phosphates.

The use of chlorine and fluorine containing aromatics with phosphate esters to produce fire-resistant fluids is claimed in Shell patents.^{26, 27, 28} The compositions consist of four materials as follows: a trialkyl phosphate in which each alkyl radical has from 4 to 9 carbon atoms, a triaryl phosphate containing a total of 18 to 33 carbons per molecule, a viscosity index improver which is a polymerized ester of hexyl to hexadecyl methacrylate having a molecular weight of at least 25,000 and a chlorofluoromethyl benzene having a boiling point above about 170°F and a pour point below about 23°F.

Various patents cover the use of phosphate esters to improve the lubricating properties of silicone fluids. A liquid homogenous silicone lubricating composition⁶⁶ having improved lubricating and fire-resistant properties can be obtained by blending liquid dimethyl silicone polymers, monoalkyl diaryl phosphates (the aryl groups consisting of phenyl, tolyl, and xylol, and the alkyl group containing 4 to 10 carbon atoms), and trialkyl phosphates (in which the alkyl groups have 4 to 10 carbon atoms). The trialkyl phosphate is required to make the monoalkyl diaryl phosphate compatible with the silicone polymer.

The incompatibility of silicone oils with petroleum hydrocarbon lubricating oils can be eliminated by the use of trialkyl phosphates (4 to 10 carbon atoms per alkyl group) in which both materials are miscible.⁶⁷ Such products have improved lubricity. The use of trialkyl phosphate alone (3 to 10 carbon atoms per alkyl group) is said⁶⁸ to increase the anti-seize lubricating properties of liquid dimethyl silicones.

The addition of tricresyl phosphate in amounts up to 35 per cent is claimed⁶⁹ to increase the lubricating properties of a mixture of aromatic hydrocarbon and silicone polymers of from 25 to 1000 centistoke viscosity.

The next group of fluids consists of mixtures of phosphate esters with esters, alcohols, glycols, ethers, and hydrocarbons. An instrument lubricant consisting of dibutyl phthalate, tributyl phosphate, and a polymerized mixture of octyl and decyl esters of methacrylic acid has been claimed.⁶⁹

Mixtures of tributoxyethyl phosphate or tributoxyethoxyethyl phosphate or tricresyl phosphate with aliphatic alcohols, glycols, or glycol

ethers are claimed⁶⁴ as synthetic lubricants. The use of tall oil soaps, inhibitors, and antioxidants together with a small amount of water is recommended.

Fire-resistant functional fluids comprising a mixture of dialkyl monoaryl phosphate esters and dialkyl esters of aliphatic dicarboxylic esters are claimed⁶⁵ to be useful as synthetic lubricants, damping fluids, grease bases, hydraulic fluids, and filter media for air conditioning systems. The viscosity characteristics of the mixtures are lower than would be predicted at low temperatures.

A timepiece lubricant of low pour point and minimum tendency to spread from the lubricating surfaces can be obtained by blending tricresyl phosphate, monoethyl ether of ethylene glycol ricinoleate, and triethylene glycol di-2-ethylbutyrate.⁶⁸ Addition of a small amount of a "dicyclic amine soap" of isoamyl octyl acid orthophosphate gives the lubricant rust-preventative properties. An electric clock lubricant which has a relatively low viscosity change over a wide temperature range, is chemically stable to oxidation and polymerization changes, and is inert to materials used in clock manufacture can be prepared from tricresyl phosphate, dibutyl phthalate, and di-2-ethylbutyl diglycolate.⁶⁶

An instrument lubricant consisting of tricresyl phosphate and di-2-ethylbutyl diglycolate with other additives has also been proposed.⁶⁵ A lubricant for electrical relays and instrument bearings utilizes tricresyl phosphate, tributyl phosphate, and ethylene glycol monobenzyl ether.⁶⁴

Hydraulic fluids of low density which are substantially fire-resistant can be prepared from trialkyl phosphates and polyhydric alcohols.³⁸ Single phosphate esters containing 1 to 8 carbon atoms or a mixture of such esters in which the total number of carbon atoms is 6 to 24 may be used. Polyalkylene glycols can be used as viscosity-improving additives.

A German patent²⁴ discloses several mixtures which are claimed to be noncorrosive and fire resistant with high boiling point and low melting point. Typical mixtures include: 61 parts tricresyl phosphate with 22 parts diphenyl oxide and 5 parts of diphenyl; 30 parts of diphenyl oxide with 61 parts of tricresyl phosphate; and 55 parts of tricresyl phosphate and 45 parts of alpha-chloronaphthalene. This patent also mentions diphenyl methane as an additional blending compound.

Hydraulic fluids⁶² having satisfactory properties at low temperatures, corrosion resistance, and low flammability can be obtained by combining a petroleum bright stock having a viscosity index of at least 60 with a trialkyl phosphate containing at least 18 carbon atoms per molecule. The bright stock should have an aromatic hydrocarbon content of less than 15 per cent and a viscosity of 1,250–11,000 SUS at 100°F. The preferred trialkyl phosphates have 6 to 12 carbon atoms in each alkyl group. The addition of a

metallic salt of a condensation product of formaldehyde with an alkylphenol is especially effective for the prevention of corrosion under oxidizing conditions.

Another patent⁷⁷ claims a mixture of a mineral lubricating oil and an ester formed by the reaction of phosphorus oxychloride with the crude product obtained from a copolymer of propylene or butylene in the "Oxo" process.

The phosphate esters, because of their good lubricating characteristics, have been used as the fluid base for synthetic greases and as additives in other base stocks which have been formulated into greases. For example, a lubricating grease can be prepared from a mineral oil, a lithium soap, and a phosphate ester such as tricresyl, triphenyl, or tributyl phosphate.¹⁶ These greases are claimed to retain their structure at temperatures of 400–500°F.

Many additives designed to improve the characteristics of the phosphate esters have been suggested. Thus, viscosity index improvers, antioxidants, corrosion inhibitors, foam inhibitors, etc. have been described. The literature on this subject is quite voluminous and will not be reviewed in this chapter. It should be pointed out that additives which are successful in modifying the properties of hydrocarbon oils may or may not have the same activity in phosphate ester fluids or in phosphate ester-containing fluids. It is, therefore, necessary to determine the activity in the particular fluid under study.

MILITARY FLUIDS

One military specification, MIL-H-19457 (Ships),⁵³ has been written for a phosphate ester lubricant and hydraulic fluid. This product was developed through the cooperation of the Navy and synthetic fluid suppliers to minimize potential fire problems resulting from certain operating characteristics of catapult systems and deck-edge elevator systems on aircraft carriers. The characteristics given in specification MIL-H-19457 (Ships) are summarized briefly in Table 4.16.

COMMERCIAL PRODUCTS

Of the commercial producers of phosphate ester-type synthetic lubricants and hydraulic fluids, three should be mentioned as having a full line of products. These are the Monsanto Chemical Company, the Celanese Corporation of America, and E. F. Houghton and Company. Characteristics of their products are given based upon their technical bulletins.

TABLE 4.16. FIRE RESISTANT SHIPBOARD HYDRAULIC FLUID SPECIFICATION.

Property	Requirement
Specification number	MIL-H-19457 (Ships)
Title	Hydraulic fluid, fire resistant
Type	Phosphate ester
Nominal temperature range	to 250°F
Specific gravity	1.14*
Density, lb/gal	9.5*
Viscosity, cs	
at 210°F	4.8 min
at 100°F	43–50
Pour point, °F	0 max
Neutralization number	0.1 max
Volatility	
Evaporation, ASTM	0.5% max 210°F
Oxidation and Corrosion	
Test temp., °F	130
Test time, hours	168
Steel	+0.2
Aluminum	±0.2
Others	0.2 mg/cm max weight loss of brass and zinc
Hydrolytic stability	
Temp., °F	200
Time, hours	48
Copper wt. loss mg/sq cm	0.2
Neut. no. fluid	0.05
Acidity water layer	10 mg KOH max
Viscosity change, %	–5 to +20 at 130°F
Insolubles, % max	0.5
Foaming (ASTM D892-46T)	
75°F (after 5 min blowing with air)	Measure
75°F (after 10 min settling period)	300 ml max
Shear stability	
Cycles pumped	5000
Temp., °F	100
Pressure, psig	1000
RPM	3600
Pump	Pesco
Requirement	10% vis. decrease at 120°F
Flammability	
General level	Fire resistant
Other tests	Must pass pipe compression ignition test; must be no indication of combustion at compression ratios of 40:1 in standard CFR cetane rating engine.

(continued)

TABLE 4.16. (CONTINUED)

Property	Requirement
Lubrication tests	Ball bearing lubrication—the Modal life of angular contact ball bearings lubricated by fluid shall be at least 50% of life using M.S. 2110 II hydrau- lic fluid.

*Typical properties.

"SKYDROL" FLUIDS

The "Skydrol"* series of fire-resistant fluids was developed in conjunction with Douglas Aircraft company primarily for use aboard transport aircraft. Fluids were designed to overcome the hazards of flammable hydraulic fluid coming in contact with hot brakes, exhaust manifolds, or other ignition sources if a line break or leakage occurred. The two "Skydrol" fluids now sold are "Skydrol" 7000 and "Skydrol" 500A. Typical properties are given in Table 4.17.⁸⁶

The "Skydrol" fluids are based on phosphate esters containing small amounts of various additives necessary to give the properties required by the stringent requirements of aircraft hydraulic systems.

"Skydrol" 7000 is the older of the two fluids. It is used both as a hydraulic fluid and as a lubricant in the cabin air supercharger system which pressurizes and furnishes breathing air, as well as in the main hydraulic system.

"Skydrol" 500A was designed to provide better low temperature characteristics than were available with "Skydrol" 7000. The 500 and 7000 refer to the viscosity of the fluid in centistokes at -40° F. "Skydrol" 500A has been adopted by many airlines as the standard hydraulic fluid for the current jet-powered transport fleets. The specific aircraft include: the Douglas DC-8, the Boeing 707 and 720, and the Convair 880 and 600. In addition, many manufacturers of airplanes in foreign countries have adopted "Skydrol" 500A for use in hydraulic systems.

Both "Skydrol" fluids meet or surpass the fire-resistant characteristics specified in AMS-3150B or MIL-F-7100. The fire resistance of the "Skydrol" fluids has been proved by actual performance. Many instances of hydraulic-system failures which could have resulted in fire did not do so when the fluid involved was "Skydrol" 7000 or 500A.

*Trademark of Monsanto Chemical Company.

TABLE 4.17. TYPICAL PROPERTIES OF "SKYDROL" FLUIDS.

Property	
Appearance	Clear, green fluid
Odor	Mild, pleasant
Autogenous ignition temperature, °F	1060
Pour point, °F	Below -70
Neutralization number	0.18 maximum
mg KOH/gm	0°C, 1.098
Specific gravity	15.6°C, 1.086
General formula	120°C, 1.003
Viscosity, cs at 210° F	4.00
at 100° F	15.7
at -40° F	7000
at -65° F	-
Viscosity index	160
Nominal temperature range	Suitable for continuous opera- tion -40° to 225° F
Thermal conductivity, Btu/hr/ft./° F at 82° F	0.0723
Specific heat, Btu/lb./° F	90 to 120° F, 0.42
Bulk modulus, psi	328,000
Foaming, ASTM standard test	Essentially nonfoaming
Shear stability	Exceeds MIL-0-5606
Surface tension, dynes/cm	28.9
Vapor pressure at 120° C, mm	0.20
Hydrolytic stability	Skydrol 7000 and Skydrol 500A are not seriously affected by low concentrations of water (less than 2%), but water contamination should be avoided.
"Skydrol" 7000	
"Skydrol" 500A	
Clear, purple fluid	Mild, pleasant
Above 1100	Below -85
0.15 maximum	0°C, 1.081
25°C, 1.065	121.3°C, 0.978
$d_4 = 1.0806 - 8.49 \times 10^{-4} t$	(gm/ml at t°C)
3.92	11.5
500	2500
238	238
Suitable for continuous opera- tion -65° to 225° F	0.0777
73° F, 0.38	145° F, 0.41
214° F, 0.44	308,000
Essentially nonfoaming	Comparable to MIL-0-5606
30.8	0.40
28.9	0.20
Skydrol 7000 and Skydrol 500A are not seriously affected by low concentrations of water (less than 2%), but water contamination should be avoided.	

The lubricity of these fluids has proven excellent in actual use. The fluid operating time in the cabin pressurization system of the DC-6 and DC-7 series of airplanes was increased from approximately 250 hours to well over 4000 hours when "Skydrol" replaced the previously used petroleum oil.

"PYDRAUL" FLUIDS

The "Pydraul"* fluids were designed to fulfill the need for fire-resistant hydraulic fluids and lubricants for industrial machinery. The requirements of hydraulic fluids for such applications are different and much less severe than those of aircraft systems.

The properties of the various "Pydraul" fluids are given in Table 4.18.^{82, 83, 84, 85}

The first "Pydraul" fluid introduced, "Pydraul" F-9, is now employed in nearly every major type of die-casting machine as well as in a wide variety of other types of equipment. "Pydraul" F-9 has never been the contributing factor in a hydraulic fire.

The "Pydraul" fluids F-9, 150 and 625 have found widespread utility in a diverse range of applications as fire-resistant hydraulic fluids. Their lubricating ability permits successful operation in gear, vane, and piston pumps. The three fluids provide a range of viscosities resulting in satisfactory operation in nearly all types of industrial machinery.

"Pydraul" AC was formulated as a fire-resistant lubricant for air compressor systems to reduce the threat of explosions possible with petroleum oil. Field performance has proven its ability to reduce hazardous residues in air compressor systems to an absolute minimum or to eliminate them completely. By minimizing residues, "Pydraul" AC effectively reduces the threat of compressor fires and explosions. In addition, it is fire resistant, and will not contribute to a fire.

The "Pydraul" fluids are fully formulated products. A major component is a phosphate ester. Other components include chlorinated hydrocarbons plus additives required to give the desired characteristics to the finished fluid.

"CELLULUBE" FLUIDS

The Celanese Corporation of America through its Chemical Division markets a series of phosphate ester fluids under the trademark "Cellulube." Six specific fluids are available: "Cellulube" 90, "Cellulube" 150, "Cellulube" 220, "Cellulube" 300, "Cellulube" 550 and "Cellulube" 1000. The numerical suffix indicates the viscosity in SUS at 100°F.

*Trademark of Monsanto Chemical Company.

TABLE 4.17. (CONTINUED)	
Property	"Skydrol" 7000
Low temperature stability	No separation or sludging at low temperatures.
Refractive index, n_D^{25}	1.470 to 1.475
Thermal coefficient of expansion	0.000452/°F 0.000753/°C
4-Ball data, scar diameter, mm	0.251
Steel-on-steel	0.586
1 kg	0.424
40 kg	1.113
Steel-on-bronze	0.327
1 kg	0.894
40 kg	0.154
0.809	
No separation or sludging at low temperatures.	
"Skydrol" 500A	

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The typical properties of the "Cellulube" series of products are given in Table 4.19.⁷⁸

The various "Cellulube" fluids are recommended for specific types of service. "Cellulube" 90 is suggested for hydraulic applications requiring low viscosity and good low-temperature characteristics. "Cellulube" 150 is recommended for applications in a variety of hydraulic systems requiring low viscosity fire-resistant fluids and in air compressors as a lubricant. "Cellulube" 220 is recommended as a general purpose industrial hydraulic fluid and air compressor lubricant. Furthermore, it is used by the U.S. Navy in the hydraulic system of deck-edge elevators on aircraft carriers where fire resistance and reliable service life are essential. It is said to be a superior sealant lubricant for vacuum pumps. "Cellulube" 300 is a medium viscosity fire-resistant hydraulic press fluid. "Cellulube" 550 is suggested for those installations requiring even higher viscosity fluids, and for larger air compressors. "Cellulube" 1000 is the highest viscosity-fire resistant hydraulic fluid available, and is for use in equipment involving large clearances.

Certain of the "Cellulube" fluids are recommended as air-compressor lubricants.⁴⁷ These lubricants reduce dangers from explosion by decreasing the accumulated carbon deposits normally formed when petroleum oils are used and by allowing only fire-resistant vapors in the compressed-air stream. "Cellulube" fluids have found use in reciprocating compressors, in non-reciprocating compressors, in rotary compressors, and in centrifugals because of the excellent lubricity of the phosphate esters.

"HOUGHTO-SAFE" FLUIDS

E. F. Houghton and Company markets a line of phosphate ester fire-resistant hydraulic fluids and lubricants under the trademark "Houghton-Safe." These materials are primarily phosphate esters. The properties of these fluids are given in Table 4.20.⁸¹

The "Houghto-Safe" fluids are recommended for the same types of uses as the "Cellulube" and the "Pydral" fluids. "Houghto-Safe" 1120 and 1055 are specifically recommended as fire-resistant air compressor lubricants.⁸⁰

The technical bulletins published by the fluid suppliers give considerably more information concerning the properties and the uses of their products than have been reported in the preceding tables and paragraphs above. Literature and technical salesmen of suppliers should therefore be consulted for detailed recommendations concerning utility, compatible components, and operating conditions. The adoption of a phosphate ester fluid for use in a system previously operated on a different type of fluid requires certain conversion procedures. These involve such items as

TABLE 4.18. TYPICAL PROPERTIES OF "PYDRAUL" FLUIDS.

TABLE 4.18. TYPICAL PROPERTIES OF	
Property	
Viscosity, SUS, 50°F	—
75°F	—
100°F	355
130°F	—
210°F	54
Viscosity index	32
Bulk modulus × 10 ⁻³ (room temp., 1000-3000 psi)	387
Compressibility × 10 ⁻⁶ , in ² /lb	2.58
Coef. of thermal expansion × 10 ⁻⁴ /°F (between 80 and 400°F)	4.1
Specific gravity, 75°F	1285
Specific heat at 77°F, Btu/lb/°F	0.32
Thermal conductivity, Btu/hr/ft/°F	0.067
at 82°F	—
at 178°F	Negligible
Solubility in water	0.2
Solubility of water in "Pydraul," %	0.6
210°F	0.1
Vapor pressure, mm Hg at 200°F	> 1100
Autogenous ignition temperature, °F	0.15 max
Neutralization number	—5
Pour point, °F	—55

TABLE 4.19. TYPICAL PROPERTIES OF	
Property	
Viscosity, SUS, 50°F	—
75°F	—
100°F	175
130°F	—
210°F	58
Viscosity index	319
Bulk modulus × 10 ⁻³ (room temp., 1000-3000 psi)	2.58
Compressibility × 10 ⁻⁶ , in ² /lb	4.2
Coef. of thermal expansion × 10 ⁻⁴ /°F (between 80 and 400°F)	1125
Specific gravity, 75°F	0.40
Specific heat at 77°F, Btu/lb/°F	0.072
Thermal conductivity, Btu/hr/ft/°F	0.064
at 82°F	—
at 178°F	Negligible
Solubility in water	0.5
Solubility of water in "Pydraul," %	0.1
210°F	0.09
Vapor pressure, mm Hg at 200°F	> 1100
Autogenous ignition temperature, °F	0.15 max
Neutralization number	—55
Pour point, °F	—

TABLE 4.20. TYPICAL PROPERTIES OF	
Property	
Viscosity, SUS, 50°F	—
75°F	—
100°F	950
130°F	—
210°F	58
Viscosity index	375
Bulk modulus × 10 ⁻³ (room temp., 1000-3000 psi)	2.58
Compressibility × 10 ⁻⁶ , in ² /lb	4.0
Coef. of thermal expansion × 10 ⁻⁴ /°F (between 80 and 400°F)	135
Specific gravity, 75°F	0.28
Specific heat at 77°F, Btu/lb/°F	0.065
Thermal conductivity, Btu/hr/ft/°F	—
at 82°F	—
at 178°F	Negligible
Solubility in water	0.18
Solubility of water in "Pydraul," %	0.55
210°F	0.4
Vapor pressure, mm Hg at 200°F	> 1100
Autogenous ignition temperature, °F	0.15 max
Neutralization number	—
Pour point, °F	—

Physical properties					
Carbon residue, Ramsbottom (ASTM D524-52T), wt %	0.71	0.65	0.61	0.88	0.77
Surface tension, du Nouy ring (ASTM D971-50), dynes/cm	43.03	41.12	40.23	40.94	41.85
Interfacial tension (ASTM D971-50), dynes/cm at 68°F	21.54	23.50	24.48	22.31	20.47
Lb/gal at 68°F	10.0	9.7	9.5	9.6	9.8
Solubility, water in, at 23°C, wt %	0.58	0.48	0.61	0.81	0.84
Solubility in water, at 23°C, wt %	0.012	0.006	0.002	0.001	0.001
Chemical properties					
Hydrolysis, 16 hr boiling water, mg KOH/g	Trace	Trace	Trace	0.08	0.06
Neutralization No. (ASTM D974-54T), mg KOH/g, max	0.1	0.1	0.1	0.1	0.1

TABLE 4.19. TYPICAL PROPERTIES OF "CELLULUBE" FLUIDS.

Lubricity					
Shell 4-ball wear test at 1 kg load, scar diam mm, avg	0.22	0.25	0.20	0.15	0.16
Shell 4-ball wear test at 40 kg load, scar diam mm, avg	0.55	0.62	0.54	0.55	0.61
Specific heat at 107°C, cal/g/°C					
Typically 0.4174 for all of the series					
Thermal conductivity at 94°C, cal/sec/cm/°F					
Typically 3.04×10^{-4} for all of the series					
Evaporation loss (ASTM D972-51T), 22 hr at 210°F, wt %	0.091	0.262	0.042	0.042	0.036
Coefficient of thermal expansion $\times 10^{-4}$ cc/cc/°F	3.4	5.8	6.3	6.6	7.6
Boiling point, interpolated at 10 mm Hg, °F	495	509	529	541	549
Boiling point, extrapolated at 760 mm Hg, °F	757	776	770	772	779
Sulfur content, wt %	<0.001	<0.001	<0.001	<0.001	<0.001

thorough cleaning, flushing, and checking of the system to be sure that compatible components are present. Again, the technical literature and the company salesmen supplying the new fluid should be consulted for conversion details.

CONCLUSION

The tertiary phosphate esters are a diverse and interesting group of chemical compounds. The esters vary widely in their physical and chemical characteristics depending upon the organic groups attached to the phosphate moiety. Both alkyl and aryl groups can be present.

The various properties of the phosphate esters have been outlined. Summarized briefly, the oxidative stability of most phosphate esters is quite good and the thermal stability is excellent at medium temperatures but becomes poor at higher temperatures. Hydrolytic stability ranges from very good to poor. Phosphate esters have excellent chemical solvency properties resulting in ready mixture with other materials. For these same reasons, they are also good solvents for some resins, paints, and many elastomers. However, a number of rubber and plastic materials have been found which are compatible with phosphate esters. Volatility of the phosphate esters is quite low. Viscosity of the phosphate esters varies over a wide range and the viscosity-temperature characteristics can be classified as medium to good.

The outstanding plus properties of the phosphate esters are their ability to lubricate moving surfaces and their fire resistance. It is these two properties that have led to widespread use of phosphate esters in the synthetic fluids and lubricants area.

The phosphate esters have found use as the sole, or major, component of synthetic lubricants and hydraulic fluids. They are used in additive amounts in both synthetic lubricants and petroleum oils. The commercial use of phosphate esters as synthetic lubricants has been primarily in the air compressor lubrication field and the hydraulic-fluid field; in particular, the fire-resistant hydraulic-fluid area. These uses have grown rapidly over the past few years and it is expected that the use of phosphate esters as synthetic lubricants will steadily increase.

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Grade	"Houghto-Safe" 1010	"Houghto-Safe" 1120	"Houghto-Safe" 1055
Viscosity, SUS 100°F. 210°F.	90	227	560
Specific Gravity 60°F.	1.20	1.15	1.22
Flash Point, °F.	505	480	505
Fire Point, °F.	670	690	680
Auto-Ignition, °F.	Over 1200	Over 1200	Over 1200
Pour Point, °F.	-30	-5	+20
Foam Tendency	Trace	20 ml	20 ml
Foam Stability	0	0	0

TABLE 4.20. PHYSICAL PROPERTIES OF HOUGHTO-SAFE FLUIDS.

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CHAPTER 5

Dibasic Acid Esters

W. G. DUKE AND A. H. POPKIN*

INTRODUCTION

The types of dibasic acid esters which are used as synthetic lubricants result from reacting straight chain dibasic acids, such as sebacic with primary branched alcohols such as ethyl hexanol. Aliphatic diesters, like aromatic diesters (e.g., dioctyl phthalate), are widely used as plasticizers, but their superior viscosity properties over a wide temperature range make them particularly useful as lubricants for aircraft engines.

In applications where high film-strength lubricants are called for, higher molecular weight complex esters—made by linking dibasic acids through a polyglycol center—are uniquely suitable. Blends of complex esters and dibasic acid esters—together with suitable antioxidants, antiwear additives and viscosity improvers—are used to formulate aircraft gas turbine engine lubricants satisfying U.S. and British military and commercial specifications.

Although the predominant use of dibasic acid esters is in jet engine lubricants, outlets for these synthetics in low-temperature greases, gear instrument oils and hydraulic fluids are growing. The advanced lubricants needed in the future will, in all likelihood, employ carefully selected diesters and complex esters to meet the stringent and unusual performance demands of supersonic jet aircraft.

HISTORY

It might be said that ester lubricants for the Jet Age of the 60's were born in the snows before Stalingrad in the winter of 1941-42. The German war machine was stalled, its trucks, machine guns and aircraft immobilized by an intense cold wave that turned lubricants into thick jelly. This disastrous experience caused the Nazi high command to accelerate research

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